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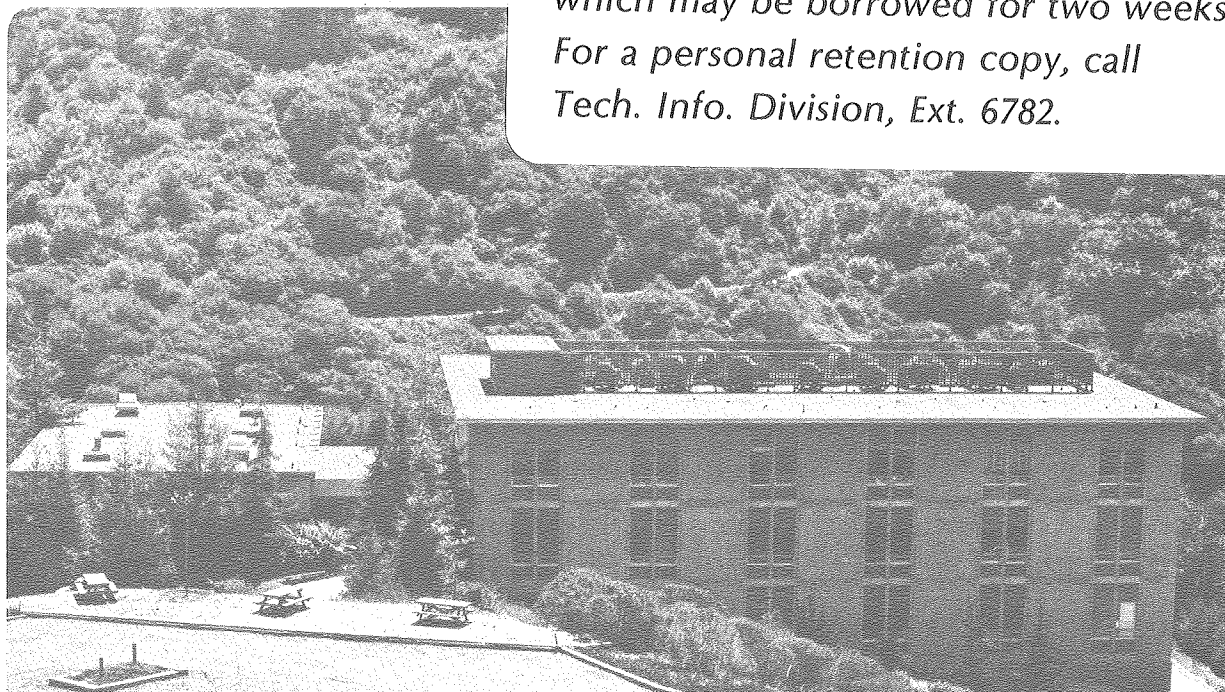
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OXYGEN INDUCED DISSOLUTION AND SEGREGATION OF SILICON
IN PLATINUM SINGLE CRYSTALS

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ABSTRACT

The segregation of silicon in platinum flat (111), stepped (553) and (332) surfaces is studied as a function of crystal temperature. Silicon segregates below 1000°C with an activation energy between 17 and 20 Kcal/mole. In the retarding field mode, the maximum amount of segregated Si corresponds to a Si (93 eV)/ Pt (242 eV) Auger peak ratio of about 5. In the presence of O₂, Si dissolves into the bulk at T \approx 600°C. The rate of Si dissolution increases with O₂ pressure and crystal temperatures. For P_{O₂} = 2.5x10⁻⁷ Torr, the activation energy for the dissolution process is 16 \pm 2 Kcal/mole. Continued exposure to O₂ results in the reappearance of Si at the Pt surface as a new phase, SiO_x, characterized by Auger peaks of Si (84 eV) and O (515 eV).

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Intruduction

There have been a considerable number of studies on the interaction of oxygen and platinum single crystals (1-10). On Pt(111) crystal surfaces a physisorbed molecular state was observed below -150°C (8,9) and two forms of atomically bound oxygen. One is a chemisorbed species that desorbs in the range of $300-500^{\circ}\text{C}$, and the other is a more strongly bound oxygen desorbing at temperatures in excess of 900°C . This last form of oxygen was shown to be located below the Pt surface by the use of ion scattering spectroscopy (13). This strongly bound oxygen has also been associated with the formation of surface platinum oxide (4) that exhibits novel chemisorption and catalytic properties (7,8,14,15).

The presence of oxygen at the platinum surface may also have profound effects on the surface concentration and solubility of other elements such as Si, C, Al, Mg, and Ca. Since these elements are often present in important platinum catalyst systems, as constituents of the high surface area supports for the finely dispersed particles of the noble metal, their behavior, when dissolved in platinum, is of considerable interest. Oxygen is also an important component of these catalysts systems as part of the oxide support. It is also utilized often for the catalyst preparation and 'activation' to obtain optimum reactivity and selectivity.

In this report we explore the dissolution and surface segregation of Si in Pt single crystals, and show how its behavior is profoundly influenced by the presence of oxygen. The solubility of Si is increased, in the presence of low partial pressures of oxygen ($\sim 10^{-6}$ Torr), by the simultaneous dissolution of oxygen in platinum, followed by the precipitation

of SiO_x at the surface under appropriate experimental conditions.

Strongly bound oxides at the surface of noble metals have been reported for Pt(4-8), Rh (20), Ir (21), and Pd (22). While the conditions of their formation can be strongly influenced by the presence of other elements as Si and Ca, that are often present in these metals in small amounts, their properties are distinctly different from the properties of SiO_2 and CaO that can segregate to the surface of the noble metals under proper conditions.

The reason for the thermodynamic stability, structure and composition of these noble metal surface oxides will be discussed in a subsequent paper.

Experimental

The Pt single crystals used in this study were cut from Pt single crystal rods furnished by Metals Research Corp. The crystals cut from these rods showed large concentration of Si segregated on the surface after heating in vacuum (16).

All the experiments were performed in standard UHV chambers evacuated with ion pumps. The surface analysis techniques used were low energy electron diffraction (LEED), and Auger electron spectroscopy (AES). The latter was performed with the LEED optics operated in the retarding field mode (RFA).

Results

In Figure 1 the amount of Si is shown detected by AES at 93 eV on the surface of a Pt(111) crystal as a function of temperature. Segregation

of Si is observed to occur on cooling below 1000°C, while dissolution into the bulk occurs on heating above 600°C. The hysteresis effect observed is due to imperfect equilibration of Si in the surface and bulk of platinum, especially at the lower temperatures. If the Pt crystal was heated long enough to permit equilibration of Si between the surface and the bulk, the hysteresis is eliminated. From the data obtained by experiments of the type shown in the figure, a segregation energy can be obtained by use of the Langmuir-McLean isotherm (19). Its value varied between 17 and 20 Kcal/mole, depending on the value taken for the Si/Pt Auger peak ratio that corresponds to $\theta=1$. This peak ratio varies in the range of 4.6 to 5.6, depending on the crystal studied (see Figures 1 and 3). An important observation is the inhomogeneity of the surface concentration of segregated Si. A scanning AES map of the Si peak intensity shows important variations as a function of position in the surface of the crystal.

To study the effect of oxygen on the surface concentration of silicon, we exposed the platinum samples that show various Si surface concentrations to a given partial pressures of O_2 . The effects of oxygen exposures are shown in Figure 2 in the case of a Pt(553) surface. The absolute peak-to-peak height of the Si (93 eV) Auger transition is plotted, in arbitrary units, as a function of time for two different O_2 partial pressures. The Si peak intensity decreases exponentially with time and the rate of this decrease depends both on the O_2 pressure and on the substrate temperature. The temperature dependence is illustrated in Figure 3 in the case of a Pt(332) crystal for a fixed O_2 partial pressure of 2.5×10^{-7} Torr. As we can see, the rate of decrease of the Auger peak intensity at 93 eV that

is proportional to the Si dissolution rate, increases with sample temperature. From the three curves of Figure 3, an activation energy of 16 ± 2 Kcal/mole for this process can be obtained. During this stage, no oxygen peak could be detected with our AES system, indicating the simultaneous dissolution of oxygen in the bulk of platinum. The removal of the O_2 molecules from the gas phase resulted in the reappearance of the Si (93 eV) peak.

Once all the Si disappeared from the Pt surface by dissolution in the bulk of the crystal, the surface can be maintained free of Si if the sample is rapidly quenched to room temperature, even after the removal of oxygen from the gas phase. The diffusion rate of Si in the Pt bulk is slow enough at low temperatures to prevent reequilibration of Si between the bulk and the surface of the metal. Continued heating of the Pt crystal in oxygen, however, causes the sudden reappearance of Si at the surface that is accompanied by the appearance of oxygen as well, as indicated in Figure 3.

The Si Auger peak is at 84 eV, however, instead of at 93 eV, and the oxygen Auger peak is at about 515 eV. These Auger peak energies indicate that this new species is silicon oxide, SiO_x ($1 \leq x < 2$) that has been detected by other studies as well (23,24). The induction time for the appearance of the segregated SiO_x , after complete oxygen induced dissolution of the Si increases with decreasing temperature as shown in Figure 3. If the gas phase O_2 is removed, while maintaining the crystal at the same high temperature, the SiO_x phase undergoes marked changes. It appears that it decomposes as indicated by the increase of the elemental Si Auger peak at 93 eV and the simultaneous decrease of the peaks at 84 eV and 515 eV

due to SiO_x . The rate of this decomposition process depends on the crystal temperature being faster at the higher temperatures.

Discussion

The segregation of Si to the surface of Pt single crystals was reported by the authors in a previous paper (16) and also by others (17,18,25). There is good agreement in the reported segregation temperatures in all these studies. Also, the total amount of segregated Si below 600°C is similar if allowance is made for the different sensitivities of the RAF and cylindrical mirror analyzer detection technique (for detection using CMA the sensitivity increases linearly with electron energy).

Although the measured activation energies for the segregation (17-20 Kcal/mole)(Figure 1) and oxygen induced dissolution (16 ± 2 Kcal/mole)(Figs. 2 and 3) are similar, they are not the result of the same process, we believe. In the segregation experiments every point of the experimental curve of Figure 1 corresponds to an equilibrium value, except those corresponding to temperatures below 600°C , where the cooling and heating curves are dissimilar due to incomplete equilibration between segregated and bulk dissolved Si as explained in the previous section. On the other hand, even at the high temperatures used in the oxygen induced dissolution of Si, the times involved are much longer than those required for equilibration during the segregation of Si in the absence of oxygen. Moreover, as seen in Figure 2, this time depends strongly on the oxygen pressure. This seems to indicate that processes other than the diffusion of Si are determining the dissolution rate. One such process may be a reaction of the type $\text{Si} + \text{O} \rightarrow \text{SiO}_x$ or $\text{Si} + \text{O} + \text{Pt} \rightarrow \text{SiO}_x \text{Pt}_y$. This would provide a sink for Si

in the bulk that decreases its concentration and therefore more Si from the surface could dissolve to keep the new equilibrium concentration values. Accumulation of SiO_x would finally result in its segregation to the surface, as observed by the appearance of the 84 eV Auger peak of Si and the Auger peak of oxygen at 515 eV.

Our value for the activation energy for Si surface segregation differs markedly from that reported by Bonzel et al.(17). This discrepancy is not understood at present.

Conclusions

1. Silicon, when present in Pt crystals, segregates to the metal surface at temperatures in the range of 600–1000°C. The measured segregation energy is found to be between 17 and 20 Kcal/mole. The maximum ratio of Auger intensities of Si at 93 eV and Pt at 242 eV is found to be close to 5.

2. Heating the Pt crystal with segregated Si on its surface in O_2 at temperatures above 600°C results in an oxygen induced dissolution of Si and later on in the segregation of an oxidized species, SiO_x , with Auger peaks at 84 eV and 515 eV, the activation energy for this process being 16 ± 2 Kcal/mole at an O_2 pressure of 2.5×10^{-7} Torr.

Acknowledgement

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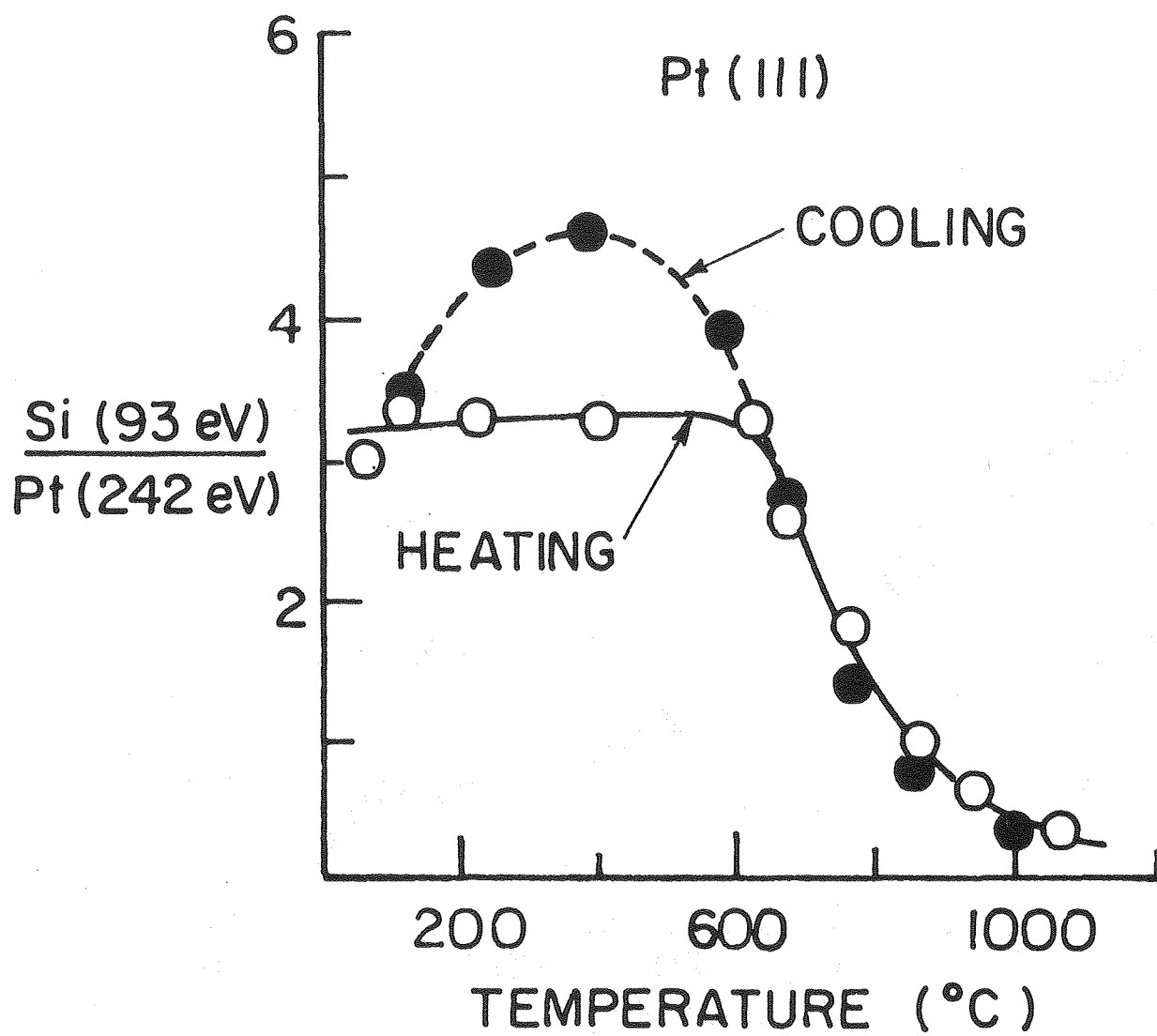
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Figure Captions

Figure 1. Concentration of surface silicon in a Pt(111) sample, as measured by the ratio of Si to Pt Auger peaks. Hysteresis is observed at low temperatures due to insufficient equilibration time.

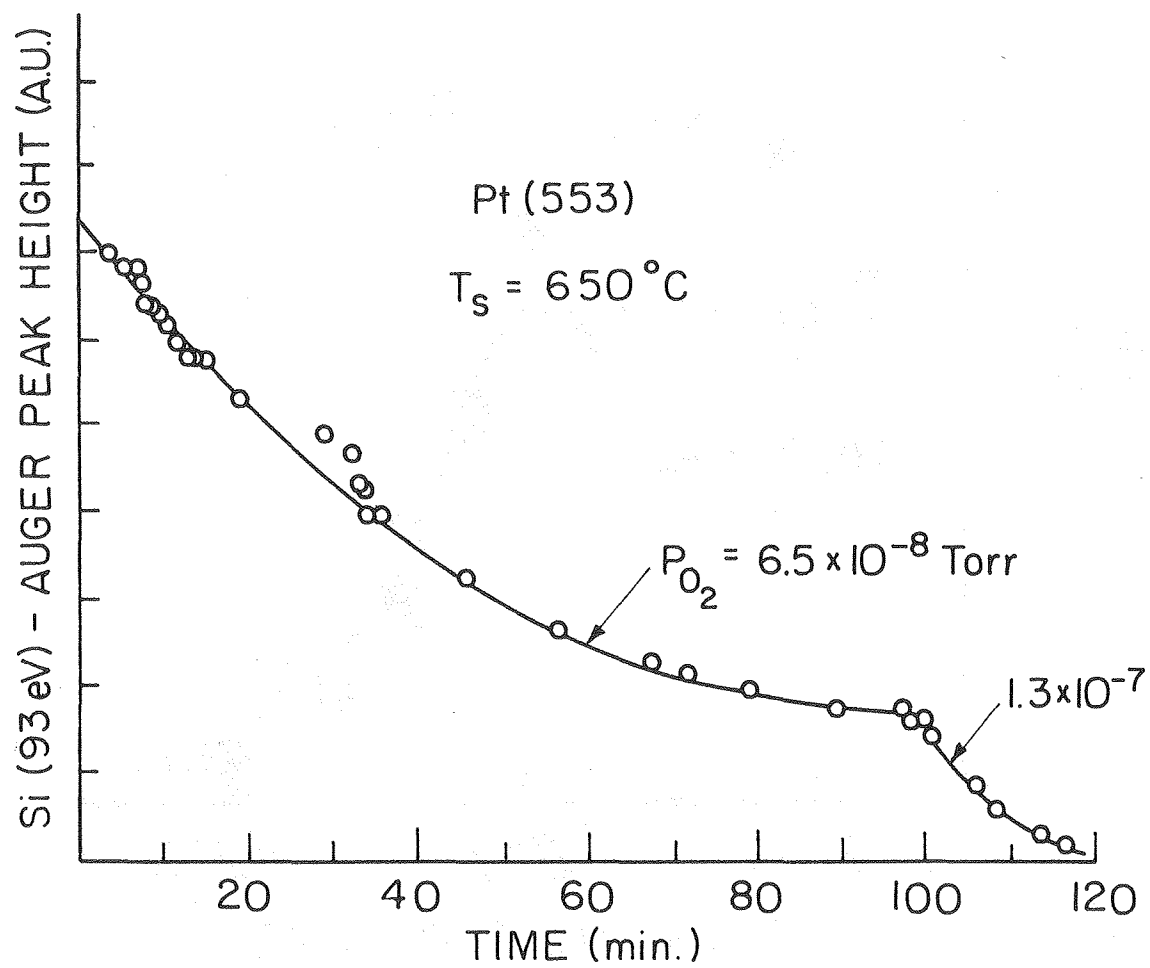
Figure 2. Decrease of surface Si concentration as a function of time, for two different O_2 partial pressures. The crystal is Pt(553) at a fixed temperature of $650^\circ C$.

Figure 3. Decrease of surface Si in a Pt(332) crystal as a function of time and for three different crystal temperatures. The O_2 partial pressure is fixed at 2.5×10^{-7} Torr. After an induction time, which is short at $750^\circ C$ and too long to be seen here at $600^\circ V$, SiO_x segregates with continued exposure to oxygen.



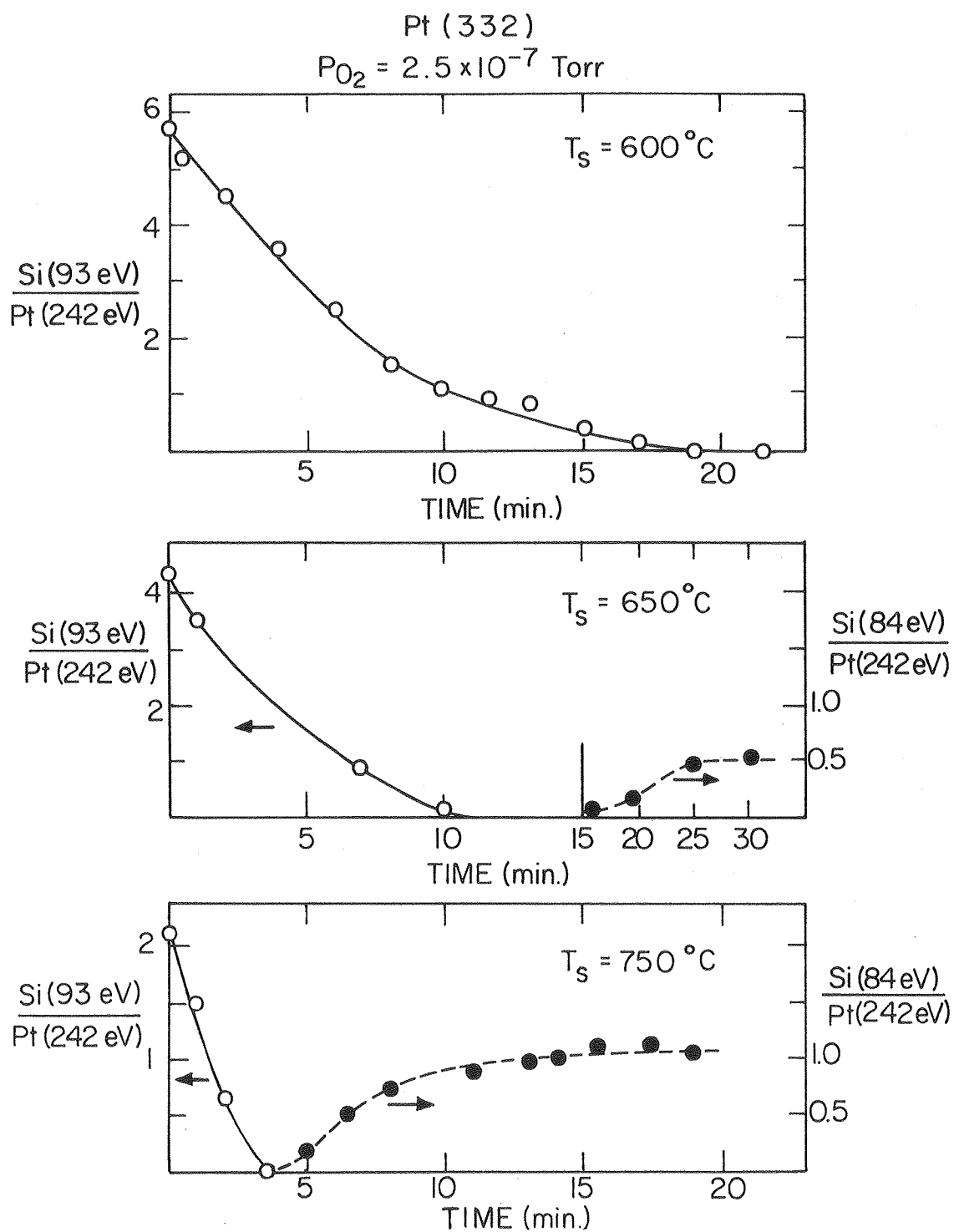
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Fig.1



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Fig. 2



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Fig.3

